Electrochimica Acta 277 (2018) 30–40

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical conversion of CO_2 to HCOOH at tin cathode in a pressurized undivided filter-press cell

Federica Proietto, Benedetto Schiavo, Alessandro Galia, Onofrio Scialdone*

Dipartimento dell'Innovazione Industriale e Digitale - DIID - Ingegneria Chimica, Meccanica, Informatica, Gestionale, Università degli Studi di Palermo, Viale delle Scienze Ed. 6, 90128, Palermo, Italy

ARTICLE INFO

Article history:
Received 29 December 2017
Received in revised form
22 March 2018
Accepted 22 April 2018
Available online 24 April 2018

Keywords:
Electrochemical reduction
CO_2 reduction
Scale-up
Pressure
Formic acid

ABSTRACT

The electrochemical reduction of carbon dioxide to formic acid was performed for the first time in a pressurized filter-press cell with a continuous recirculation of the electrolytic solution (0.9 L) at a tin cathode. It was shown that the performances of the system are comparable or slightly better than that of a batch system with a smaller volume (0.05 L). The selection of proper values of both current density and CO_2 pressure allowed to achieve quite high values of faradaic efficiencies. Long-time electrolyses have shown that the system is stable and that it can allow to generate quite high concentrations of HCOOH (about 0.4 M).

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

In the last years, an increasing attention has been devoted to the electrochemical conversion of CO_2, which could combine the utilization of excess electric energy from intermittent renewable sources with the selective conversion of CO_2 into added value products [1–3]. CO_2 can be selectively converted by electrochemical reduction into various useful chemicals by changing the operative conditions of the electrolysis [4,5]. To date, researches have shown that several products, including carbon monoxide [6,7], formic acid, methane, methanol [8,9], ethylene and oxalic acid [10], can be obtained by this process [11]. This wide variety of chemicals depends on many operative conditions of the electrochemical process such as the choice of the nature of the working electrode [12,13], the electrolytic solution [14], the cell design, the working potential, etc … Furthermore, it has been shown that carbon dioxide can be introduced in the backbone of other molecules, generating fine chemicals with high economic value, such as anti-inflammatory drugs, by cathodic reduction in aprotic solvents [15–19]. Considering the products listed above, one of the more promising chemicals produced by CO_2 electrochemical reduction in water is the formic acid, which is more close to the large-scale industrial application despite some disadvantages have to be overcome. Formic acid is an important intermediary in the chemical and pharmaceutical industry; in particular, it is mainly used as antibacterial agent in industrial feed, in the cotton and food disinfection, in the natural rubber production, and in the formation of acid baths for the dyeing processes of fibres and leathers [20–22]. Among the many encourage factors, the price of HCOOH (1300 \$/ton with an estimation of an annual increase of about 2% [22]) was much higher than other products (i.e. CH_3OH: 400 \$/ton) and it is also considered a good H_2 storage medium [21]. However, its energy density (i.e. HCOOH: 2.1 kWh L^{-1}) is lower than the other CO_2-derived products (i.e. CH_3OH: 43.3 kWh L^{-1}) [23], limiting its application as fuel [14,20]. In addition, the electrochemical path to HCOOH generation is simple and straightforward and has a smaller environmental impact than the current production process [20,24,25]. Formic acid is electrochemically produced in aqueous solution at specific cathodes as indium, lead, mercury and tin, which are characterized by high hydrogen over-potential allowing the stabilization of several steps for HCOOH generation [13,26]. In particular, Pb and Sn cathodes seem an excellent choice because they allow to obtain the formic acid with high FE. Their large-scale use was evaluated by many authors, that concluded that only for the Sn electrode there is an interesting engineering and economic feasibility, thanks its low cost and its no toxicity [27–29].

---

* Corresponding author.
E-mail address: onofrio.scialdone@unipa.it (O. Scialdone).

https://doi.org/10.1016/j.electacta.2018.04.159
0013-4686/© 2018 Elsevier Ltd. All rights reserved.

Furthermore, it has been recently shown that the economics of the process can be drastically improved coupling the cathodic reduction of CO_2 with a suitable anodic process that add value to the system (such as the anodic purification of wastewater) [21]. Electrochemical conversion of CO_2 into formate/formic acid on Sn electrode was studied under different operative conditions in water [27,30–36]. It was shown that the main hurdle of the reduction of carbon dioxide from water solution is the low solubility of CO_2 in water (0.034 M). To overcome this obstacle, several approaches were developed. One of these is the utilization of gas diffusion electrodes (GDEs) obtaining FE to formate/formic acid up to 75% [1,24,37]. As an example, Del Castillo et al. [38] have achieved a 70% of FE and formate concentration of about 55 mmol L^{-1} at 150 mA cm^{-2} by CO_2 electro-reduction in a divided filter-press type cell equipped with GDE. Another simple strategy is to increase the CO_2 pressure: indeed, enhancing the CO_2 solubility in water improves the performances of the electrochemical process allowing to work at high current density which is very important at the industrial level [39]. Recently, it has been shown that an increase of the pressure leads to a drastic enhancement of the final formic acid concentration. In particular, high concentrations of formic acid (>0.46 mol L^{-1}) with relatively good FE was achieved, working at relatively high CO_2 pressures (15–30 bar), at high current density (>90 mA cm^{-2}) and with a cheap and simple batch undivided cell [40].

In spite of these good and promising results, some steps have to be done to better evaluate the process from an applicative point of view: in particular, the scale-up in a filter-press cell under pressure have to be done and the stability of the system has to be evaluated for longer times. Indeed, up to now the carbon dioxide reduction in filter-press cells was evaluated only at room pressure and most of experiments reported in the literature concern quite low amounts of time (from few minutes to few hours) and of the charge passed [25,41,42]. Hence, in this work the electrochemical reduction of CO_2 was evaluated in a simple undivided filter-press cell with 0.9 L of electrolytic solution at cheap tin cathodes under pressure (1–30 bar). The effect of various operating parameters, such as the current density, the flow rate and the pressure, was investigated in detail, allowing to find very promising operating conditions for the production of formic acid. Furthermore, the performances of the process were evaluated for many days for an amount of charge passed up to about 70 kC.

2. Experimental

2.1. Reagents and analyses

An electrolytic solution composed of bi-distilled water as solvent and 0.1 M Na_2SO_4 (Janssen Chimica) as supporting electrolyte has been employed. The initial pH of the solution was fixed at 4 using H_2SO_4 (Sigma-Aldrich) in order to obtain acid solutions, according to our previous work [40]. To feed the system, CO_2 (99.999% purity) supplied from Rivoira was employed. Agilent HP 1100 HPLC fitted with Rezex ROA-Organic Acid H^+ (8%) column (Phenomenex) at 55 °C and coupled with a UV detector working at 210 nm was used to evaluate the formic acid concentration. The used mobile phase is a 0.005 N H_2SO_4 water solution at pH 2.5 eluted at 0.6 mL min^{-1}. A pure standard of formic acid (Sigma-Aldrich) was adopted to calibrate the instrument for its quantitative determination. Agilent 7890 B GC equipped with a Carboxen-1000 (60/80) column and a Thermal Conductivity Detector (at 230 °C) was used to analyse the gas composition. Helium (Air Liquide 99.999% purity) was used as carrier gas with constant pressure set at 1 bar; the column temperature program was an isotherm at 35 °C for 5 min followed by a 20 °C/min ramp up to 225 °C and by an isothermal step for 45 min.

2.2. Electrolysis

The experimental system was constituted of a continuous recirculation reaction system (Fig. 1a) equipped by: I) a pressurized undivided filter-press cell with parallel electrodes (shown in detail in Fig. 1c); II) a centrifugal pump (MicroPump GHA-V21 with a maximum power pumping of 200 mL min^{-1}); III) a stainless steel tank equipped with three connecting lines in the top: one for the CO_2 input, one for the products gas phase output and one connected with the bottom line for the circulation of the liquid phase; IV) a parallel line to the tank, equipped with a view-cell to check the liquid level in the system. The system was equipped with a pressure gauge and a pressure relief valve used to regulate the operative pressure; each connection is made in an AISI 316 stainless steel. CO_2 was fed to the system at a flow of 100 mL min^{-1} pressurizing the system. A continuous circulation of distilled water washed the system after each experiment. The overall arrangement of the pilot reactor is shown in Fig. 1b. The system volume is more of 1 L. The cell was equipped with a tin sheet cathode (metallic tin foil RPE, assay ≥ 99%, supplied by Carlo Erba) and a $Ti/IrO_2–Ta_2O_5$ sheet anode (commercial DSA from ElectroCell AB); the electrodes gap was 0.5 cm. The current density was computed as the ratio between the current intensity and the wet surface area of the tin cathode exposed to the anode (i.e. 9 cm^2). The anode was polished by ultrasound bath in distillate water. Since Sn electrode could be affected by degradation and/or deactivation under cathodic polarizations [31], after each test, the tin cathode was subjected to mechanically smoothing treatment, chemically pre-treated with a water solution of 11% HNO_3 (Romil Chemicals) for 2 min and, subsequently, cleaned with an ultrasound bath in distillate water for 5 min before each test. The volume of the loaded electrolytic solution was 0.9 L for most of electrolyses and 0.5 L only for the experiment aimed to evaluate the time effect. Electrolyses were performed under amperostatic mode (Amel 2053 potentiostat/galvanostat) at room temperature. Experiments were repeated at least twice, giving rise to reproducibility within 5% of the results. The faradaic efficiency (FE) and the instantaneous faradaic efficiency (IFE) were defined, as follows:

$$FE = 2\,F\,V\,[FA]_t / I\,t\ ;\ IFE = 2\,F\,V\,\left([FA]_{t+\Delta t} - [FA]_t\right)/I\,\Delta t$$

where F is the faradaic constant (96487 C mol^{-1}), V the solution volume, $[FA]_t$ the concentration of formic acid at the time *t* and *I* the current intensity.

The thickness of the stagnant layer in the adopted condition was defined through a well-know diffusion limiting current technique using a very stable redox couple (i.e., Fe^{2+}/Fe^{3+}). The electrolytic solutions were constituted of aqueous solutions with the same concentrations of $K_4Fe(CN)_6$ thrihydrate 99% (Carlo Erba reagents) and $K_3Fe(CN)_6$ 99% (Merk) (20, 40 and 80 mM). The diffusion coefficient *D* values in water were assumed of: i) 6.631 10^{-10} $m^2\,s^{-1}$ for this couple [43,44]; ii) $1*10^{-9}$ $m^2\,s^{-1}$ for the formic acid; and iii) $1.94*10^{-9}$ $m^2\,s^{-1}$ for the CO_2 [45].

3. Results and discussion

Several series of electrolysis were performed in a continuous recirculation system equipped with a filter-press cell (described in Section 2.2) to evaluate the effect of several operative parameters on the figures of merit of the CO_2 electrochemical reduction to HCOOH. In the first stage, in order to individuate the best operative process conditions, a detailed study on the effect of the CO_2 pressure, current density and flow rate was carried out using a plate Sn

Download English Version:

https://daneshyari.com/en/article/6602737

Download Persian Version:

https://daneshyari.com/article/6602737

Daneshyari.com